

# Heavy going

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Chiral symmetry breaking is imaged in graphene which, through a mechanism analogous to mass generation in quantum electrodynamics, could provide a means for making it semiconducting.

Thanks to the presence of Dirac points in the electronic band structure, graphene can host emergent quasiparticles that behave as massless Dirac fermions. But engineering a sizeable mass for the Dirac fermions in graphene is important for a range of technological applications as it would open up a bandgap and turn graphene into a semiconductor. Writing in *Nature Physics*, Christopher Gutiérrez and colleagues<sup>1</sup> now experimentally show how a bandgap at the Dirac points can be opened by breaking an effective chiral symmetry.

The asymptotic and distinctive  $\nabla$ -shaped density of states near the Dirac points of graphene protect them against weak electron-electron interactions. So what mechanisms are available for opening a bandgap? For pristine graphene, Semenoff<sup>2</sup> predicted that a charge-density wave, which penalizes the occupancy of electrons in one triangular sublattice of the underlying honeycomb lattice with respect to another, could open a bandgap at the two inequivalent Dirac points<sup>2</sup>. Haldane showed that a gap could also be opened by breaking time-reversal symmetry<sup>3</sup>.

But a third mechanism is that of a bond-density wave<sup>4</sup>, which breaks neither time-reversal symmetry, nor the conservation of electronic charge. This instability was christened a Kekulé bond-density wave because it breaks the  $n/3$  rotation symmetry of the honeycomb lattice down to  $2\pi/3$ , just as the Kekulé bond-density does in the benzene molecule<sup>4</sup>.

Cheianov et al. proposed the following microscopic mechanism to open a Kekulé gap in graphene<sup>5,6</sup>. The enlarged unit cell of graphene with the Kekulé pattern can be pictured by tiling the honeycomb lattice with a three-colour code; say red, blue and green. If a dilute density of adatoms is then randomly placed on the graphene at high temperature, the system would minimize its free energy by optimizing two free-energy gains against one free-energy loss below some ordering temperature<sup>5,6</sup>.

An electronic energy is gained by opening a Kekulé bandgap at the two inequivalent Dirac points of graphene. An effective two-body interaction between adatoms is also gained by occupying a fraction of the sites of the honeycomb lattice assigned one of the three colours. This effective two-body interaction is mediated by the Dirac fermions of graphene when the chemical potential matches the energy of the Dirac points. Elastic energy is lost by displacing the carbon atoms so as to

form the short and long bond lengths that characterize the Kekulé bond-density wave.

Although a Kekulé instability has been observed in artificial graphene<sup>7</sup>, realizing and observing such bond-density waves in pristine graphene has proved challenging experimentally, partly because of incommensurate phenomena encountered when using proximity effects.

Using scanning tunnelling microscopy (STM)-based techniques, Gutiérrez et al. show that the microscopic mechanism previously proposed<sup>5,6</sup> to open a Kekulé gap can work at temperatures extending up to 300 K (see Ref. 1). They achieve this by growing graphene epitaxially onto Cu(111) (see Ref. 8) in such a way that all of the copper atoms just below the graphene are in registry with the carbon atoms. However, as there are fewer copper atoms than carbon atoms, some carbon atoms have no copper atoms below them. It is these vacancies that play the role of the adatoms in the scenario described in refs 5 and 6. Gutiérrez et al.<sup>1</sup> call these vacancies ghost adatoms and their ordering is called ghost Kekulé order. Such order opens a bandgap at the Dirac point, and imparts a mass on the Dirac fermions.

From the point of view of effective field theories, the dynamical generation of a fermionic mass through the spontaneous symmetry breaking of an emergent chiral  $U(1) \times U(1)$  symmetry down to its unbroken  $U(1)$  electromagnetic charge symmetry group is the same mechanism as that advocated in a seminal paper by Nambu and Jona-Lasinio in 1961<sup>9</sup> to explain the origin of the nucleon masses.

Unlike the Haldane mass that supports edge states along lines at which the corresponding order parameters vanish, the Dirac masses that encode the Kekulé ordering come in pairs. As such they support vortex-like defects that bind zero modes<sup>4</sup>. This phenomenon is accompanied with a fractionalization of quantum numbers, say a fractional charge if the electronic spin is polarized<sup>4</sup>. There should be points in the STM field of view where three distinct Kekulé domains meet, thereby creating vortex-like defects, and so it should be possible to experimentally probe the associated localized states with fractional quantum numbers.

A final caveat to note is that copper is metallic, so it shorts any transport (or lack thereof) in the graphene, which means that this is perhaps not the perfect system for device applications. But this is certainly a promising first step towards endowing graphene with transport

properties that can be tuned from the semimetallic to the insulating regimes.

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